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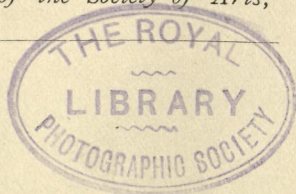

CANTOR LECTURES

ON

PHOTOGRAPHIC CHEMISTRY,

BY

PROF. R. MELDOLA, F.R.S.

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PHOTOGRAPHIC CHEMISTRY.

BY

PROF. R. MELDOLA, F.R.S.

LECTURE I.—DELIVERED MARCH 9, 1891.

Apart from the popularity of photography as an inexpensive amusement, enabling the amateur to obtain with comparatively simple appliances permanent records of places visited, or representations, more or less faithful, of the features of those whose individuality it is wished to bear in remembrance, the subject is becoming of daily increasing importance on account of the numerous applications which photographic processes have found, both in art and in science. For this reason it is desirable that the claims of photography to be considered a distinct branch of applied science or technology should be urged upon all those who are in any way interested in the advancement of technical education. Some progress has already been made in this direction in certain schools and colleges in this country, but when our efforts are compared with the keen appreciation of the subject which is borne witness to by the splendidly equipped photochemical laboratories of the technical high schools of Berlin and Vienna, it will be admitted that in this, as in other departments of chemical technology, we have allowed ourselves to sink into a secondary position. It is certainly remarkable that the land of Fox Talbot and Herschel—the country which has given to the photographic world all the most important processes discovered since the foundation of the

art by Niepce and Daguerre*— should nowhere possess a school of photo-chemistry where the subject can be taught from a scientific platform, or where original investigators can find the requisite appliances and the skilled assistance necessary for the prosecution of research.

Setting out from the admission that photography must, sooner or later, become incorporated in all schemes of systematic instruction in applied science, I propose in the present course of lectures to show how this subject may be dealt with from a chemical point of view. From this it must not be inferred that photography is to be regarded purely as a branch of chemical technology, for it has also its physical side, and the highly trained photographer should be well grounded in the theory and construction of lenses, spectrum analysis, and, in short, in the general principles of optics. Assuming this knowledge to have been acquired, we may proceed to ask how the subject is to be taught, and the considera-

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* This is no vain boast. Taking the discoveries in order, we have the silver print and chromatised gelatine emanating from Fox Talbot; the cyanotype due to Sir John Herschel; the collodion process introduced by Scott Archer and Fry; collodion dry plates by Russell; printing with pigmented gelatine worked out by Swan; gelatino-bromide emulsion introduced by Maddox; and the platinotype process of Willis; to say nothing of the photo-mechanical printing processes, such as Woodburytype, to which English investigators have contributed so largely.

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tion of this question is of considerable importance—it is, in fact, of far greater importance than may appear at first sight, for photography is most admirably adapted to bring out into prominence the principles of technical instruction in a subject which is very largely of a chemical nature. The consideration of this question may help to dispel some of the haze with which the much-abused term " technical training " has been surrounded, and it will certainly lead to a clear conception of the object and scope of these lectures.

There are many who identify technical instruction with the teaching of some handicraft, a notion which has no doubt arisen from the identification of technical skill with manual dexterity in some mechanical industry. By the adoption, either tacitly or openly, of this narrow definition, the chemical industries have suffered to a very large extent in this country, because their progress is more dependent on a knowledge of scientific principles, and much less dependent on manual dexterity than any of the other subjects dealt with in schemes of technical instruction. Now in order to give technical instruction in a subject like photography, which is so intimately connected with chemistry, we may adopt one of two courses. The student may become a practical photographer in the first place, and may then be led on to the science of his practice by an appeal to the purely chemical principles brought into operation. This may be called the analytical method. The other method is to give the student a training in general chemistry first, and then to specialise his knowledge in the direction of photography. This may be regarded as a synthetical method.

In other departments of technology, and especially in those where the underlying principles are of a mechanical nature, the analytical method may be, and has been, adopted with success. It is possible to lead an intelligent mechanic from his every-day occupations to a knowledge of the higher principles of mechanical science by making use of his experience of phenomena which are constantly coming under his notice. From this it is sometimes argued by those who are in the habit of regarding technical instruction from its purely analytical side, that technical chemistry can be taught by the same method. Some teachers may possibly succeed in this process, but my own experience, both as a technologist and a teacher, has led me to the conclusion that, for chemical subjects, the analytical method is both too cumbersome and circuitous

to be of any real practical use. No person engaged in chemical industry in any capacity —whether workman, foreman, manager, or proprietor—can be taught the principles of chemical science out of his own industry, unless he has some considerable knowledge of general principles to start with. No person who is not grounded in such broad principles can properly appreciate the explanation of the phenomena with which his daily experience brings him into contact, and if his previous training is insufficient to enable him to understand the nature of the changes which occur in the course of his operations, he cannot derive any advantage from technical instruction. These remarks will, I hope, serve to emphasise a distinction which exists between technical chemistry and other technical subjects, and I have thought it desirable to avail myself of the present opportunity of calling particular attention to this point, because it is one which is generally ignored in all discussions on technical education.

The reason for this difference in the mode of treatment of chemical subjects is not difficult to find. The chemical technologist—the man who is engaged in the manufacture of useful products out of certain raw materials—is, so far as the purely scientific principles are concerned, already at a very advanced stage, although he may not realise this to be the case. The chemistry of manufacturing operations, even when these are of an apparently simple kind, is of a very high order of complexity. There are many branches of chemical industry in which the nature of the chemical changes undergone by the materials is very imperfectly understood; there is no branch of chemical industry of which the pure science can be said to be thoroughly known. For these reasons I believe that I am justified in stating that the chemical technologist is working at a high level, so far as the science of his subject is concerned, and this explains why he cannot be dealt with by the analytical method.

The general considerations which have been offered, apply to the special subject of photography with full force. A person may become an adept as an operator without knowing anything of physics or chemistry; there are thousands of photographers all over the country, who can manipulate a camera and develop and print pictures with admirable dexterity, who are in this position. If we adopt the narrow definition of technical instruction, we should appoint such experts in

our colleges, and through them impart the art of taking pictures to thousands of others. But would our position as a photographing nation be improved by this process? I venture to think not. We might be carrying out the ideas of certain technical educators by adopting this method, but I do not imagine that in the long run the subject itself would be much advanced; our position in the scale of industry would not be materially raised by the wholesale manufacture of skilful operators. And so with all other branches of applied chemistry; it is technologists whose knowledge is based on a broad foundation that are wanted for the improvement of our industries. These are the men which are raised in the technical high schools of the Continent, and whose training the continental industries have had the wisdom to avail themselves of.

To become a photographic technologist, as distinguished from a photographer, it is desirable, therefore, that the student should have received instruction in the general elementary principles of physics and inorganic and organic chemistry. When thus prepared, he may begin to specialise his studies, and the real technical training will be commenced. The application of chemistry to photography will naturally divide itself into two branches: the chemistry of the materials used in the art, and the theory of the chemical changes occurring in photographic processes. This last part of the subject I have already attempted to deal with, to some extent, elsewhere.* With respect to the chemistry of photographic materials, time will not admit of any attempt to draw up a complete code of instruction. Nor is this necessary on the present occasion, for the requirements will be met by the simple statement that this branch of the subject should be an extension of the ordinary chemical training, with special reference to the preparation, properties, and reactions of the compounds which the student is most likely to have to deal with in photography.

In so far as the study of the chemistry of photographic materials is ordinary text-book knowledge, it is not proposed, therefore, to take up your time by unnecessary recapitulation; but certain special reactions, having a direct bearing on photographic processes, may be worth dwelling upon. Since the compounds of silver are by far the most important of photographic chemicals, it will be advisable to commence with these. After a study of the ordinary qualitative reactions of this metal,

* "The Chemistry of Photography," Macmillan, 1889.

the student should be well practised in the quantitative estimation, both gravimetrically and volumetrically, so that the value of commercial silver nitrate may be ascertained with precision. The reducing action of fused sodium carbonate, of zinc and acid, and of alkaline solutions of glucoses on the silver haloids, can be made the basis of practical exercises in the recovery of silver from residues. It is desirable also to point out, and to illustrate by experiment, that silver is displaced from the solution of its salts by the more electro-positive elements—hydrogen, copper, mercury, iron, zinc, lead, and so forth. It is important also to demonstrate that silver is more electro-positive than gold and platinum, and displaces these metals from solutions of their salts.

In illustrating such points in the chemical history of silver as those referred to, and, in fact, in all practical work leading from ordinary chemistry to photographic chemistry, it will be found advantageous to adopt the general principle of performing the experiments, whenever practicable, both in glass vessels and on films. This method is admirably adapted to lead the student from the general science to its special application to his subject. For example, having shown that the salts of silver are reduced by such reducing agents as alkaline pyrogallol, ferrous sulphate, &c., in test-tubes, and having allowed the experimenter to convince himself that the precipitate in these cases is really metallic silver, the production of a film of the metal may be shown by taking a sheet of paper coated with silver nitrate, and, when dry, painting stripes of ferrous sulphate solution on the coated surface. On washing out the excess of nitrate from the unreduced portions, it will then be realised that the dark stripes consist of finely-divided silver on a paper surface. With these silver films many instructive demonstrations can be given. Thus, the fact that silver displaces gold and platinum from solutions of the salts of these metals may be shown by passing the paper through a bath of platinic or auric chloride, when the silver stripe undergoes a change of colour, indicating the replacement of that metal by gold or platinum. A comparison of the strip thus treated with a portion of the original strip—by treating both with nitric acid—clearly proves that the platinised stripe has lost its solubility in that acid. The application of this principle to toning and intensification will naturally follow, when photographic processes are being dealt with.

While demonstrating the reducibility of silver salts by such reagents as ferrous salts, &c., it must be strongly urged that reduction of the silver salt is accompanied by a corresponding oxidation of the reducing agent. This fact will be made apparent by the chemical equations; but it is important that the student should verify it experimentally. Many ways of doing this will suggest themselves, but it will be sufficient if I give one appropriate example. Every student may be assumed to be familiar with the different behaviour of ferrous and ferric salts towards potassium ferrocyanide. Now, on adding a solution of ferrous sulphate to a solution of silver nitrate we get a precipitate of silver, indicating the reduction of the silver salt. That a simultaneous oxidation of the ferrous salt takes place is proved by filtering off the silver and adding ferrocyanide to the solution, when Prussian blue is at once formed. An apology is really necessary for detaining you with such a well-known illustration, but the broad principle that chemical reduction is accompanied by a simultaneous oxidation, is so important in photographic chemistry, that the student cannot be too strongly impressed with its generality.

The precipitation of finely-divided silver may be made use of to illustrate some of the more obscure phenomena with which the photographic chemist is frequently confronted. It is desirable to point out that outside the domain of text-book science there is a mass of information concerning the properties of silver which may become of direct importance in connection with photographic processes, and the consideration of which will certainly help to broaden the student's notions of his subject. It may be well at this stage to broach the idea that photographic chemistry, like all other branches of applied chemistry, does not begin and end with a series of reactions which can be written down in the form of equations. This mode of treating the subject may be academic but it is not technical. It is believed by many experimenters that silver is capable of existing in several different conditions of physical aggregation according to the manner in which it is precipitated from its solutions. Thus the deposit obtained by adding ferrous sulphate to a solution of silver nitrate is grey; the product obtained by reducing silver solutions with organic ferrous salts is darker in colour.* It

is possible that the difference of colour in these cases may be due, as suggested, to the differences of molecular aggregation. The rate of reduction may have something to do with it, and the well-known coloured forms of precipitated gold, studied by Faraday, may be referred to in this connection.

But, on the other hand, there is another possibility, which must be borne in mind and well emphasised in dealing with photographic chemistry. I allude to the tendency which silver and its compounds possess, in common with many other metals, of bringing down and retaining traces of foreign substances, in whose presence the metal or its compounds may be precipitated. This kind of combination is not sufficiently recognised by orthodox chemistry, because it does not take place in definite proportions, but there are many branches of applied chemistry where this so-called molecular combination plays a very important part. The practical outcome of these considerations is that the student of photographic chemistry cannot be too early prepared for the occurrence of indefinite combination, and he must not be allowed to suppose that because a distinct formula cannot be ascribed to such compounds that they are outside the pale of chemical science. I have thought it necessary to utter this caution, because in the present state of knowledge we must not commit ourselves to dogmatic assertions about allotropic modifications of silver. It may be that the different colours of reduced silver are due to the retention of "traces" of some foreign substance. The fact that minute traces of impurity produce remarkably great changes in the physical properties of metals is now familiar through the experiments of Roberts-Austen, and we must be prepared for a similar modification in such a physical property as that of colour by the influence of associated "impurity."

In connection with this part of the subject the recent experiments of Carey Lea* demand some notice. By reducing certain organic salts of silver, viz., the citrate and tartrate, with the corresponding ferrous salts, this experimenter professes to have obtained three allotropic modifications of silver. After carefully considering the conditions of formation, and after repeating some of the experiments, I must say that there appears to me to be no sufficient evidence that these coloured forms

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* Pyrogallol will reduce silver nitrate in neutral or slightly acid solutions. It is not necessary to add alkali to show this reduction; the solution may be distinctly acid with acetic acid.

* "Amer. Journ. Sci. [3], vol. 37, p. 476, and vol. 38, pp. 47 and 129. Also "Phil. Mag.," vol. 31, pp. 238, 320, and 497.

consist of the pure metal. On the contrary, all the evidence goes to show that some impurity is present[†]; the published analyses of the products in no case show a greater percentage than 98·75 per cent. of metal. If an alloy of gold, containing only 0·2 per cent. of lead, differs so completely from pure gold as to be brittle instead of malleable and ductile; if the colours of many metals can be completely modified by being alloyed with small quantities of other metals, such, *e.g.*, as the deep purple alloy of aluminium of gold, it is not unreasonable to suppose that the colour and other properties of precipitated silver would be modified by combination with 1 per cent. or more of some impurity which may consist of an organic iron salt. At any rate, it seems premature to speak of these products as allotropic forms of silver.

The whole subject of the reduction of silver salts by various inorganic and organic reducing agents is well worthy of engaging the attention of the photographic chemist. Did time permit, I could point out many lines of investigation which might be followed up with comparative simplicity. If the student can be brought to realise that we have yet a great deal to learn about the nature and composition of these coloured products—if the spirit of inquiry can be stirred within him till he is prompted to take up the investigation of some of these compounds for himself—he is far more likely to contribute towards the advancement of photography than by taking any number of pictures. And I will add that if he has the true spirit of technology in his composition, he will derive quite as much pleasure from this kind of work as from manipulating the camera.

The haloid salts of silver will, of course, demand a considerable share of attention from the photographic chemist. The preparation and properties of these compounds should be studied in detail; their solubility in well-known reagents, such as ammonia, potassium cyanide, and sodium thiosulphate, should be made the subject of practical exercises, and the chemical changes undergone can be made readily intelligible to the student whose elementary training has reached the necessary stage of efficiency. It will add to the thoroughness of the instruction if the student is made to realise that the statement that the silver haloid is soluble or insoluble in such or such a reagent is by itself inadequate; he must understand that solubility means the formation of a new compound which is more soluble than the original haloid. Thus the absorption of ammonia by silver chloride can readily be shown by putting some of the dry haloid into a tube, weighing, and then passing dry ammonia gas till there is no further increase in weight. Then, again, silver chloride may be dissolved in strong ammonia, and the solution allowed to stand till the crystals of the ammonio-silver chloride separate. The preparation of the soluble silver sodium thiosulphate, by the method of Lenz,[*] is a good practical exercise, and the study of this salt will help to make clear why the silver haloids are dissolved by the thiosulphate. It is necessary to point out that by the same reagent three[†] distinct products may be obtained:—

1. Silver thiosulphate, $Ag_2S_2O_3$, by adding a solution of sodium thiosulphate to a solution of a silver salt, keeping the latter in excess. This is a white insoluble salt, which soon darkens by the formation of the sulphide:—

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

2. The insoluble double salt $Ag_2Na_2(S_2O_3)_2$, formed by adding silver nitrate solution to a solution of sodium thiosulphate till a permanent precipitate is formed. The product is dark-coloured, and probably contains sulphide; it gradually becomes darker on standing, owing to decomposition with the production of sulphide.

3. The soluble double salt $Ag_2Na_4(S_2O_3)_3$, formed by the action of excess of sodium thiosulphate upon the last salt, or by adding a silver salt to a strong solution of the thiosulphate, keeping the latter in excess. In the solid condition this is a white crystalline salt, readily soluble in water, and much less prone to decompose into sulphide than the preceding salt.

All this is, of course, only ordinary chemistry,

[†] Thus in repeating these experiments Prange (" Rec. Tran. Chim.," ix., 121) found that the dark substance precipitated from the solution of the so-called " soluble silver" always contained traces of iron as an impurity.

[*] A solution of silver nitrate is added, drop by drop, to a strong solution of sodium thiosulphate till a permanent precipitate (the insoluble double salt) just begins to appear. The solution is filtered and alcohol added till the white crystalline (soluble) double salt separates out.

[†] There are probably many more double thiosulphates of silver and sodium, and even this series of salts requires further investigation. Thus Mr. C. H. Bothamley informs me that by mixing 4 $AgNO_3$ with 5 $Na_2S_2O_3$ and adding alcohol, he obtained a white precipitate in which the ratio Ag : S was 1 : 1·961. The ratio calculated for $AgNaS_2O_3$ is 1 : 1·683. This salt is *soluble* and stable. By the action of 3 $Na_2S_2O_3$ on Ag Br and fractional crystallisation, he has isolated two crops of crystals corresponding with the formula $Ag_2S_2O_3$, $3Na_2S_2O_3 = Ag_2Na_6(S_2O_3)_4$.

but it must be taught, and cannot be better taught than by letting the student prepare the compounds for himself and study their properties. The utility of this knowledge will become obvious when the fixing process is dealt with.

Among other properties of the silver haloids to which attention may be directed are their decompositions by various haloid acids and salts. This information cannot but be of the greatest use in practical photography. I have summarised the facts in the form of a Table:—

Reagent.	Ag Cl.	Ag Br	Ag I
Cl	No action	Ag Cl formed	Ag Cl formed
Br	,, ,,	No action	Ag Br formed
I	,, ,,	,, ,,	No action
HCl	,, ,,	Ag Cl formed at high temperature	Ag Cl formed at high temperature
HI	Ag I formed	No action	No action
KCl	No action	,, ,,	,, ,,
KBr	Ag Br formed	,, ,,	,, ,,
KI	AgI formed	Ag I formed	,, ,,

" No action " must be taken as meaning no decomposition.

The haloid salts of the alkaline metals and of ammonia, especially when in concentrated solutions, dissolve more or less of the silver haloid, with or without decomposition. The silver haloid is thrown out again, either in an unaltered state, or transformed into another haloid by decomposition on diluting the solution with water. The solubility of the silver haloids in solutions of other salts is a feature in their chemical history which the photographic chemist will find it useful to be put in possession of. Thus these haloids are to some extent soluble, and especially the iodide, in strong solutions of silver nitrate. It must be pointed out that in all cases where a silver haloid is dissolved by another salt, a double salt is probably formed. In fact, many of these double salts have been isolated, and I subjoin a list coupled with the caution that I do not hold myself responsible for the formulæ :—

AgI,2KI and AgI,KI. Bollay, " Ann. Ch. Phys." [2], xxiv, 377.

AgCl,NH₄Cl, and AgCl,KCl. Becquerel, Gmelin's Handbook, I, 401.

AgBr,AgNO₃. Schnauss and Kremer, Jahresb., 1855, 419; Riche, *ibid.*, 1858, 207 ; Risse, *ibid.*, 1859, 229.

AgI,2AgNO₃. Weltzien, " Ann. Ch. Pharm." xcv, 127 ; Risse, Jahresb., 1859, 228 ; Stürenberg, " Arch. Pharm." [2], cxliii., 12.

AgI,AgNO₃. Schnauss and Kremer, Jahresb., 1855, 429. See also Stürenberg, " Arch. Pharm." [2], cxliii, 12.

4AgI,2Hg(NO₃)₂,H₂O. Preuss, Gmelin's Handbook, vi., 199. See also Wackenroder, *ibid.* 159 and 165; Liebig, " Ann. Ch. Pharm.", lxxxi, 128, and Debray, " Compt. Rend.", lxx, 995.

A most useful form of Table, showing the solubility of silver chloride in solutions of other chlorides is given by Hahn in Biedermann's "Chemiker - Kalender," and is here subjoined (p. 7).

Similar Tables for silver bromide and iodide would be of special value to photographic chemists.

The study of the forms of reduced silver will have prepared the way for taking into consideration the state of molecular aggregation of a substance as influencing its characters. The silver haloids should be dealt with from this point of view, both on account of the importance of bringing into prominence the factor of physical condition, and because of the possible practical bearing of the subject in connection with the preparation of sensitive emulsions. According to the mode of preparation of the haloid, such important characters as solubility, reducibility, optical absorption and colour, and photographic sensitiveness are capable of being influenced. Thus, the state of concentration of a solution of silver nitrate, from which the chloride is precipitated by hydrochloric acid, appears to influence the solubility of the chloride in the acid.* It is possible that this is due to the different forms of the chloride under these conditions. By

* Ruyssen and Varenne, "Bull. Soc. Chim." [2] xxxvi, 5. See also Ditte, "Ann. Chim. Phys." [5] xxii, 551.

SOLUBILITY OF SILVER CHLORIDE IN SALT SOLUTIONS, BY H. HAHN.

Salt.	Per-centage of Salt.	Temperature of saturation.	Per-centage of AgCl.	Per-centage of Ag.	Specific gravity.	Tempera-ture.	Grammes of Ag. per 1,000 c. c.
K Cl	24·95	19·6°	0·0776	0·0584	1·1774	19·6°	0·0688
Na Cl	25·96	19·6°	0·1053	0·0793	1·2053	19·6°	0·0956
NH₄ Cl	28·45	24·5°	0·3397	0·2551	1·0835	30·6°	0·2764
Ca Cl₂	41·26	24·5°	0·5713	0·4300	1·4612	30·6°	0·6283
Mg Cl₂	36·35	24·5°	0·5313	0·3999	1·3350	30·6°	0·5339
Ba Cl₂	27·32	24·5°	0·0570	0·0429	1·3017	30·6°	0·0558
Fe Cl₂	30·70	—	0·1686	0·1269	1·4199	20°	0·1802
Fe Cl₃	37·48	—	0·0058	0·0044	1·4472	21·4°	0·0064
Mn Cl₂	43·85	24·5°	0·1996	0·1499	1·4851	30°	0·2226
Zn Cl₂	53·34	—	0·0134	0·0101	1·6005	30°	0·0162
Cu Cl₂	44·48	24·5°	0·0532	0·0399	1·5726	30°	0·0627
Pb Cl₂	0·99	24·5°	0·0000	0·0000	1·0094	30°	0·0000

dropping a solution of silver nitrate into strong hydrochloric acid, a considerable quantity of the chloride is dissolved; according to Pierre,[*] more than 0·5 per cent. of the weight of acid. The chloride, prepared in the ordinary way, by precipitation from silver nitrate and a soluble chloride, after being washed and dried, is certainly not soluble in hydrochloric acid to the same extent. Here, again, it is possible that precipitation in the presence of strong hydrochloric acid gives no time for the molecular condensation of $(AgCl)_c$ to $(AgCl)_{nx}$, and that the former of these aggregates is more soluble than the latter. The existence of silver chloride and bromide in several modifications was, as is well known, first established by Stas;[†] but the photographic bearing of the discovery did not become apparent till the general spread of gelatino-bromide emulsion processes led to the further study of these modifications, and especially those of the bromide, by Monckhoven, Eder, Abney, and Vogel.

I have called attention to this feature in the chemical history of the silver haloids, because, in the present condition of practical photography, no student should be allowed to neglect this all-important subject. The information is

not to be obtained from the ordinary text-books used by chemical teachers; and it is instructive to note how a point of comparative insignificance in general chemical training may become exalted into importance as soon as the science becomes to be applied in a special direction. Every branch of technology abounds with illustrations of this principle. How far Stas's classification of the forms of silver bromide and chloride will stand the test of further investigation is at present doubtful.[*] Some experimenters recognise only two modifications, and others three; while Stas himself recognises four, viz. :—

1. Flocculent, white or yellow. Produced by the addition of a solution of a soluble bromide or hydrobromic acid to a solution of silver nitrate in the cold. Both solutions must be dilute (0·5 to 1 per cent.); if the silver is in excess, the bromide is white; if the soluble bromide is in excess, the precipitate is yellow.

2. Pulverulent; obtained from the preceding modification by brisk agitation with water. This form is produced more rapidly in neutral than in alkaline solutions. It is described as a yellowish-white powder, which, when dry, becomes intensely yellow on heating.

3. Granular; produced by adding a very dilute boiling solution of ammonium bromide

* "Compt. Rend." lxxiii, 1000.
† "Compt. Rend." lxxiii, 998; "Ann. Chim. Phys." V., 1874; "Chen. Centr.", 1875-81. For thermochemical confirmation, see Berthelot, "Compt. Rend," xciii, 870,

* See V. Schumann in *Chem, News*, vol. liii, p. 97.

to a boiling solution of silver nitrate containing $\frac{1}{10}$ per cent. of this salt. Obtained also by the action of boiling water on the preceding modifications, the first (flocculent) giving a dull yellowish white, and the second (pulverulent) giving a bright, yellowish white powder. By prolonged boiling with water, the granular modification gradually becomes subdivided, and after several days' boiling, forms a kind of milky emulsion, from which the bromide settles out very slowly. The precipitate which then subsides is pearly white, becoming intensely yellow on agitation with a strong solution of ammonium bromide.

4. Crystalline, or fused; obtained by fusing any of the other forms. This modification is never employed in photographic operations.

It might perhaps be suggested that the first form is an unstable hydrate, capable of existing only in the presence of water; but whatever view may be taken with respect to the actual number of modifications, the broad fact that the bromide is capable of forming different molecular aggregates possessing different colours and degrees of solubility may be regarded as highly probable. It is desirable, therefore, that the student of photographic chemistry should at any rate make some experiments in this direction in connection with his laboratory work.

Among other points in the chemical history of the silver haloids which are of photographic importance, the relative reducibility claims special notice. In the earlier part of his practical work, the student will have obtained metallic silver from the haloids by reduction, but he must now be made to realise that this reduction is more readily effected in the case of the chloride than the bromide, and more readily in the case of the latter than with the iodide. And first of all, in order that the true chemical significance of reduction may be made intelligible, let a simple demonstration be given showing that by the action of reducing agents, such as ammonium pyrogallate, potassio-ferrous oxalate, &c., the halogen is actually withdrawn from the silver, and is to be found in the solution by the usual tests. Then, in order to show that the chloride is more reducible than the bromide or iodide, a solution of potassio-ferrous oxalate may be diluted till it becomes just too feeble to reduce the bromide. Some of the same solution will be found to reduce the chloride readily. Adopting the usual course, and passing from test-tubes to films, sheets of paper coated with the three silver haloids may be streaked with the same solution of ferrous oxalate or ammonium pyrogallate,* when the order of reducibility will be shown by the fact that the chloride gives a darker stripe than the bromide, and the latter a darker stripe than the iodide. The importance of these facts will become obvious when, at a later stage, the subject of photographic development has to be dealt with from its chemical aspect.

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* The addition of some sodium sulphite is advisable, in order that the results may not be masked by the too rapid discolouration of the pyrogallate.

LECTURE II.—DELIVERED MARCH 16, 1891.

Continuing the study of those properties of silver salts which are of photographic importance, the next point to be dealt with is the vexed question of the existence of sub-salts. Here, in the present state of knowledge, it is most advisable to avoid dogmatic statements. The utmost that can be done is to summarise the evidence, and to let the student see therefrom that, from a scientific point of view, the existence of such sub-salts has not been conclusively demonstrated. To all who are familiar with the course of investigation in this direction, it will be evident that the current statements in text-books, and which are repeated in the photographic manuals, must be taught with due caution. I have no time to go over the whole of this familiar ground again, and I must content myself by giving references.* I will only repeat now what I said some years ago, viz , that so far as analogy is to be trusted as a guide, it would seem improbable that the sub-haloid salts of silver should be highly coloured compounds, because the analogous salts of copper, mercury, and thallium are not highly coloured.† Now, all the attempts which have been made to produce sub-haloid salts of silver by partial reduction or by other methods, give rise to coloured products, which have been held by some investigators to consist of the sub-haloids, and by others (Carey Lea) to consist of molecular compounds of the sub-haloids with the haloids proper. It may further be suggested that these coloured compounds might consist of oxyhaloids, mixed or combined (molecularly) with the haloids, that in some cases they might consist of metallic silver or its oxide in molecular combination with the haloid, and that in other cases they might consist of the foregoing compounds or mixtures, or of the true haloids coloured by the retention of a small quantity of some metallic oxide as an impurity.*

The study of these coloured products is of importance to the photographic chemist, whether they are definite chemical compounds or whether they are molecular compounds, or whatever subsequent research may prove them to be. They are of importance to us here, among other reasons because there may be some relationship between these compounds and the products formed by the photochemical decomposition of the silver haloids. I have thought it desirable therefore to summarise, in a collected form, the various methods by which these compounds have been produced :—

1. Rose-coloured silver chloride; obtained by reducing a hot solution of silver citrate with hydrogen, exhausting the dark product (before complete reduction) with citric acid, and then treating it with hydrochloric acid. Obtained also by reducing the dry nitrate in hydrogen at 100° C., extracting the product with water and treating the residue with hydrochloric and nitric acids. (Brit. Assoc. Rep., 1859, p. 105.)

2. Chocolate-coloured chloride; obtained by adding a solution of silver arsenite in nitric acid to a strong boiling solution of caustic soda, when "an extremely black powder" is produced. This on treatment with hydro-

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* See " Chemistry of Photography," Lecture I , pp. 39 et seq ; also Nature, vol. xlii., p. 246 (July 10th, 1890). A brief historical summary will also be found in Carey Lea's paper on the allotropic forms of silver already referred to. Some of the earliest experiments on this subject were made by Wöhler, and will be found referred to, together with much additional work, in a Report published by a Brit. Assoc. Committee, in 1859.

† Thallous iodide is yellow, and mercurous iodide greenish yellow.

* Since the delivery of the lecture, M. Güntz has contributed a paper to the "Comptes Rendus" (vol. cxii., p. 861), claiming to have isolated the sub-haloids by preparing, in the first place, the sub-fluoride by the electrolysis of a saturated solution of silver fluoride. By the action of HCl, HI, H_2S, H_2O, &c., on the sub-fluoride, the other sub-haloids, and the sub-oxide, Ag_4O, are said to have been prepared (see Nature, April 30th, 1891, p. 620). Seeing the tendency possessed by fluorine compounds to become polymerised, it is, however, by no means certain that the " sub-fluoride," which is described as a crystalline powder resembling bronze filings, has the simple formula Ag_2F.

chloric acid becomes grey, and the washed product on boiling with dilute nitric acid loses silver and leaves the chocolate-coloured chloride. (Brit. Assoc. Rep., 1859, p. 106.)

3. Coloured products obtained by acting upon silver with solutions of ferric or cupric chloride have long been known. (Becquerel's films; see G. Staats in Ber. deutsch. chem. Gesell., 1887, p. 2322, and 1888, p. 2199.)[*]

4. Coloured products obtained by Carey Lea, and described as "photochloride," "photobromide," and "photoiodide" ("photosalts").

(a.) Purple or black chloride, obtained by the action of alkaline hypochlorites on finely-divided (reduced) silver.

(b.) Red chloride, prepared by adding ferrous sulphate to an ammoniacal solution of silver chloride and then acidifying with dilute sulphuric acid. The precipitate is washed, boiled with dilute nitric acid, washed, and finally boiled with dilute hydrochloric acid.

(c.) Red, or copper-coloured chloride, prepared by heating silver oxide or carbonate to a point short of complete reduction, and then treating the residue with hydrochloric acid.

(d.) By precipitating silver oxide in the presence of the lower oxides of iron, manganese, &c., and treating the product with hydrochloric acid.

(e.) Dark purple chloride, obtained by treating finely-divided (reduced) silver with a solution of ferric-chloride. (Contains 76·07 per cent. of silver.)

(f.) Red chloride, similarly prepared by the action of cupric chloride.

(g.) Red chloride, prepared by pouring dilute solution of silver nitrate on to cuprous chloride, and boiling the black precipitate thus obtained with dilute nitric acid.

(h.) Brownish purple chloride, prepared by pouring an ammoniacal solution of silver nitrate into a strong solution of ferrous chloride, and treating the dark precipitate with dilute sulphuric acid. Becomes lighter with nitric acid. (Similar to b.)

(i.) Purple chloride, prepared by reducing the citrate in a current of hydrogen at 100° C., and treating the product with hydrochloric and nitric acids successively. (Similar to No. 1.)

(j.) Red and purple shades of chloride, obtained by reducing (partially) a silver salt with alkali and an organic reducing agent, such as milk-sugar, dextrine, &c., and then treating with hydrochloric and nitric acids successively.

(k.) Red, brown, or lavender chloride, produced by treating the white chloride with a boiling solution of sodium hypophosphite. The dark, chocolate-coloured product is washed, and boiled with dilute nitric acid.

By somewhat similar methods, coloured forms of the bromide and iodide have been obtained: but it will be unnecessary to trouble you with the details, as these will be found in the original papers. (See "Amer. Journal Sci.," vol. xxxiii., May and June, 1887, and vol. xxxiv., July, 1887.) It is quite easy for the student of photographic chemistry to repeat some of these experiments, and to prepare some of the coloured products. Especially simple are the processes b, g, h, j. The repetition of these experiments will not only be useful as practical exercises, but they will serve to enlarge the ideas of the worker with respect to such familiar compounds as the silver haloids, which, in ordinary work, are generally regarded as mere tests for the halogens, and to show him that a wide domain for exploration lies beyond the region of his ordinary chemical experience. In this connection, also, it is desirable to call attention to the tendency of the silver haloids to retain traces of other chlorides, such as those of iron (ferric), cobalt, manganese, nickel, copper, &c.[*]

From these special studies of the silver compounds we may now pass to another phase of the subject, viz., the combination of silver and its salts with organic compounds. At this stage the technology, i.e., the sources and methods of manufacture of the more important organic compounds used by the photographer may be conveniently introduced. The ordinary organic acids, such as acetic, oxalic, citric, tartaric, &c., will of course have been dealt with in the preliminary training, but in addition to these special attention should be directed to the chemistry and technology of cellulose (including paper, collodion, and

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[*] The coloured films produced by this method do not always owe their tints to the formation of a coloured product of the nature of a pigmentary colouring matter. The chromatic effect is, in many instances, purely optical, i.e., due to the phenomenon of "thin plates." The coloured spectra recently obtained by M. Lippmann are of the same nature; see Berget's "Photographie des Couleurs," Paris, 1891.

[*] Carey Lea, "Amer. Journ. Sci.," vol. xxxiv., p. 384.

celluloid), albumen, and gelatine. Let it be realised in the course of this work that albumen is of the nature of an acid forming salts with various metals. Show the precipitation caused by such salts as those of mercury and silver. Let the precipitated " albuminate " of silver be collected, washed, and dried, and then the presence of silver proved by burning some of the compound, extracting with dilute nitric acid, filtering, and testing in the usual way. The similar tendency of gelatine to combine with silver compounds is very striking, and of fundamental importance to the photographic technologist. The best way of approaching this is to let the student make experiments for himself. A sheet of gelatine can be prepared by coating a glass plate with a warm, strong solution of the substance, and allowing it to dry for some days in a warm place. When stripped off, the film is floated for some hours on a solution of silver nitrate, then removed and washed with water. It now remains to be shown that silver in some form or other has actually been withdrawn from the solution, and has entered into combination with the gelatine. In order to prove this, some of the gelatine compound can be dried, and burnt, and tested, in the same way as the "albuminate." The "gelatino-nitrate" can also be proved to darken on exposure to light. An experiment of this kind will prepare the way for the all-important subject of the preparation of emulsions.

The proportions of materials and the various technical details are fully treated of in all works on practical photography, and need no special description in these lectures.* The first point to which attention must be called is the nature of an emulsion, and the influence of the vehicle in keeping the silver haloids in suspension. An easy experiment will bring this home to the student. To a solution of common salt or some soluble bromide add some silver nitrate, and notice the immediate separation of the silver haloid on agitation. Now take some of the same salt solution, add a little strong gelatine solution to it, mix by agitation, and then again add some of the same silver nitrate solution. It will be noticed that the separation of the silver haloid takes place more slowly, and that when formed it does not subside as in the previous experiment, but agitation simply helps to make the

contents of the vessel (now an emulsion) more uniform. A similar experiment may be made with ordinary alcohol and ether containing a soluble haloid ($ZnBr_2$, or $CdBr_2$), and then, by way of comparison, with the same alcohol and ether containing dissolved pyroxylin (collodion).

By such experiments as these the principle of emulsification will be clearly brought out. The student should, in connection with these experiments, be well practised in calculating the necessary quantities of the different haloids for precipitating given weights of silver nitrate. At this stage the practical preparation of emulsions might well be commenced, and plates should be coated with gelatino-bromide emulsions, prepared in accordance with any of the adopted formulæ. This should at first be carried out with the object of imparting skill in the *technique* of the operations, the scientific reasons for having an excess of soluble bromide, and for washing out excess of soluble salts being explained in the course of the work. These explanations will of course only be fully appreciated after the action of light upon the silver haloids has been dealt with, and the practice of emulsion making can, if thought desirable, be deferred to a later period.

In the same way that the compounds of silver are prepared and studied, the other photographic materials should be dealt with. Their ordinary chemical properties should be familiar to the student, not only through reading or attending lectures, but by laboratory work. His knowledge should be as wide as possible, and should embrace the compounds of iron, chromium, manganese, uranium, copper, mercury, platinum—in short, of all the metals having any connection with photography, and, it is hardly necessary to add, that the special uses of any of these compounds in photographic processes should be dwelt upon exhaustively. To this knowledge it is desirable to add an acquaintance with the formulæ and mode of preparation of the reducing agents, both inorganic and organic, used for development, such, e.g., as hydroxylamine, pyrogallol, hydroquinone, eikonogen, and so forth.

Armed with this general chemical knowledge, specialised in the direction of his subject, the student will be in a position to proceed to the particular kinds of decomposition, viz., photochemical, upon which the art of photography is based. This part of the subject must also be dealt with as broadly as

* Abney's works are of course familiar to all practical photographers in this country. The latest edition of Dr. Eder's " Photographie mit Bromsilber-Gelatine, &c.," will be found invaluable to those who can read German.

possible, for it is of the utmost importance that the principle should be realised that the photochemical decompositions made use of in photography are but particular instances of a general class of such decompositions, some of which are at present not available for photographic purposes. It must be pointed out that a study of some of these collateral decompositions is likely in the future to lead to results of practical value, and may certainly be expected to throw great light on the nature of the photographic image.

The broad distinction between purely physical changes induced by light and actual photochemical decomposition may be maintained, although it is often difficult to refer a particular case to one or the other of these classes. Complete lists of all the known instances of the physical and chemical action of light will be found in the works of Eder and Vogel,* but it is advisable, in treating the subject as a branch of chemical technology, not to bewilder the student, at first, with a vast array of facts, but rather to enforce general principles by a few well-chosen illustrations which the student can work out for himself without much difficulty. The simplest kind of photophysical action is that which produces a change in molecular structure, either temporary or permanent. In connection with this, the action of light upon selenium is perhaps the most striking illustration that can be given, and where the necessary apparatus is at hand, it would be well to demonstrate the point experimentally in the usual way. As examples of permanent change of molecular structure, the modifications in crystalline form undergone by certain substances on exposure to light may be appealed to and illustrated. The following experiments can be easily done in the laboratory :—

1. A saturated solution of sulphur in carbon disulphide is prepared, and two or three tubes are filled with the solution and sealed up. The contents of a tube kept in the dark will remain clear for an indefinite time, but on exposing one of the tubes to sunlight, the contents become turbid, and a gradual separation of insoluble sulphur crystals will take place.

2. A plate of glass is coated with a silver mirror by any of the usual methods of chemical reduction. The mirror is iodised by exposure to the vapour of iodine,† and then exposed to

bright light (electric arc or sunlight) for 10 or 15 minutes, one portion of the film being protected by a dark paper screen. The film is semi-transparent at first, but, after the experiment, it will be found that the exposed portion has become yellower and more opaque than the screened portion, the change being apparently due to a physical modification of the silver iodide.

Such experiments as these will serve to impress the mind with the fact that light can cause purely physical changes. Attention may be called to the existence of other changes of a like nature, such as those which occur in red cinnabar, in red realgar, in the crystalline form of nickel sulphate and zinc selenate, &c. From cases of this kind we are led, in the next place, to other changes, which serve to connect photophysical with photochemical action, viz., photopolymerisation. The meaning of the term polymerisation will be familiar to the chemical student. It must be pointed out that many of the changes in crystalline form, &c., alluded to in connection with the previous examples, may be really cases of photopolymerisation or depolymerisation. Then the known cases of the polymerisation of organic compounds, such as anthracene to paranthracene, styrene to metastyrene, vinyl bromide, thymoquinone to an insoluble modification,* and so forth, may be dealt with and illustrated, as far as possible, experimentally. Pointing out, by way of caution, that it is often very difficult to discriminate between photopolymerisation and photo-oxidation, the action of light upon asphalt and bituminous substances may be taken as an illustration of the difficulty in question ; and a study of the action of light upon such films will naturally lead to the various heliographic processes based upon the original method of the elder Niepce. How far it is desirable to lead the worker in this direction from the practical side must, of course, be determined by circumstances.

The action of light upon asphalt and similar substances is not only of practical importance, but its scientific aspect is worthy of the most serious attention, both by the student and the investigator, who, after all, is himself only a student at a somewhat more advanced stage

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* Ausfuhr. Handb , Part I.; Vogel's Handb. d. Photog., Part I.

† Such films of silver haloids on glass are very convenient

for experimental purposes, as they are (when dry) absolutely free from anything that can be regarded as a sensitizer, and are therefore particularly well adapted for purposes where films of the pure haloids are required.

* H. W. Vogel has obtained a positive print in thymoquinone by making use of this property. See his " Handbuch," Part I., p. 41.

of his studies. There is some doubt at present whether the insoluble asphalt resulting from the action of light is a polymeride, or whether it is a product of photochemical oxidation. According to some authorities, the change does not take place in a vacuum, neither in nitrogen nor in hydrogen. On the other hand, it is stated by Kayser, in favour of the polymerisation theory, that no increase of weight occurs in the film, that the insoluble asphalt is converted into the soluble form again by fusion, and that a solution of asphalt in a closed vessel also deposits the insoluble modification on exposure to light. The decision of this point rests with future investigators, but certain facts have been discovered with respect to the constituents of asphalt which must be emphasised in connection with photographic chemistry. It has been found that Syrian and Trinidad asphalt contain a small quantity (4 to 5 per cent.) of a substance soluble in alcohol and insensitive to light, another portion (44 to 57 per cent.) soluble in ether, and a residue insoluble in ether, varying from 52 to 38 per cent. The portions soluble in alcohol and ether, and the insoluble residue all contain carbon, hydrogen, and sulphur; and Kayser, who has investigated these compounds, has gone so far as to assign formulæ to them. The portion which is soluble in ether is sensitive to light, but not so sensitive as the insoluble residue, which contains the constituent of the greatest value for the heliographic processes. The practical outcome of these investigations has been the preparation of a high quality asphalt, consisting essentially of the portion insoluble in alcohol and ether. It may be added that the property of becoming insoluble in hydrocarbon oils on exposure to light does not appear to depend upon the constituent containing the sulphur, as some specimens of asphalt from different parts of the world, which possess the same property, have been found, on analysis, to be free from sulphur, and to consist of hydrocarbons only.

Before leaving these facts concerning asphalt, I should like to point out that there is a promising line of investigation here, which would well repay a few years' patient work, even if it led to no practical result. I am inclined to believe, however, that the results would be of practical value, and especially in the direction of increasing the sensitiveness of the asphalt film. Asphalt is a complicated mixture of hydrocarbons, &c., and it is probable that the sensitiveness is due to a few or possibly to only one of its constituents. It would be worth while therefore to make a further series of experiments having for their object the isolation of the sensitive constituents. I need hardly pause to point out of what immense value it would be to have a bitumen film possessed of a sensitiveness approximating only to that of the silver bromide emulsion.

From these cases of photophysical action, of polymerisation, and of possible photochemical oxidation, the study of true photochemical decomposition may be taken up. On account of the comparative simplicity of their decomposition, the salts of iron lend themselves admirably for demonstration at this stage. The study of the ordinary chemical reactions of iron salts will have prepared the way. Having shown how reducing agents convert ferric into ferrous salts, let it be demonstrated experimentally that many organic compounds, such as alcohol, oxalic acid, &c., do not immediately reduce ferric salts. It must then be pointed out that these organic compounds are susceptible of oxidation by ferric salts under the influence of light—that they are in fact potential reducing agents. This can be done in test-tubes or flasks in the first place, and then on paper films, leading to the ordinary cyanotype and blue printing processes. A few hints for the carrying out of the experiments may be found serviceable :—

(1.) A solution of ferric chloride (2-3 p.c.), mixed with a solution of oxalic acid* will of course on testing with potassium ferricyanide give no blue colouration. Some of the same solution, exposed for five minutes or so to strong light, will be found to contain ferrous salt, on again testing with ferricyanide :—

$$2FeCl_3 + H_2C_2O_4 = 2FeCl_2 + 2HCl + 2CO_2.$$

2. By using ferricyanide with the ferric salt, and exposing to light, the reduction is made visible by the formation of Turnbull's blue. This can be done by adding ferricyanide to the foregoing, or preparing two solutions : one containing 8 grms. of potassium ferricyanide in 50 c.c. of water, and the other containing 10 grms. of ammonio-ferric citrate in 50 c.c. of water. The solutions are mixed before use, and then exposed to light, first in a test-tube, and then on paper coated with the solution, and allowed to dry in the dark. The practical application of this method for copying and printing will be obvious.

* The addition of some alcohol increases the sensitiveness of the mixture.

The chief point of general theoretical importance brought out by such experiments as these is, that light only reduces the ferric salts in the presence of oxidizable compounds of sufficient instability. It is advisable, at this stage, to introduce the notion of *sensitizers*, and to point out that oxalic acid, citric acid, alcohol, &c., may be regarded in this light in the experiments referred to. The demonstrations with ferric salts may, of course, be extended in many directions, and made the basis of numerous practical exercises and lessons in the application of general chemical principles to special cases. All that has to be borne in mind is, that a surface of an organic salt exposed to light under a stencilled design (or a picture) gives ferrous salt on the exposed portions, leaving the unexposed portions unchanged. Various reagents may then be used to reveal the chemical difference in the two portions, the subject of photographic development being thus introduced, and the changes involved being explained by ordinary chemistry. By way of example :—

(1.) A design printed on paper coated with ammonio-ferric citrate is developed by ferricyanide. The exposed (reduced) portions come out blue owing to the formation of Turnbull's blue. Supposing ferrous citrate to be formed :—

$$Fe''_3 (C_6H_5O_7)_2 + K_6 Fe_2Cy_{12} = Fe_3 (Fe_2Cy_{12}) + 2 K_3 (C_6H_5O_7).$$
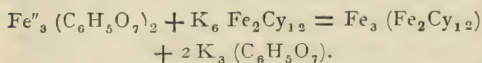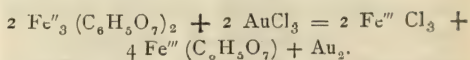
The blue design, after being well washed, can be made the subject of many further experiments, all instructive as illustrating chemical principles with which the student should be familiar. Thus, on treatment with a dilute solution of caustic soda, the blue is at once decomposed with the formation of Fe_3O_4, which remains on the paper. We have thus a faintly visible brownish design, which can again be developed by taking advantage of the property possessed by the oxides of iron of forming coloured compounds with organic substances, such as gallic acid, alizarin, nitrosophenols, &c.

(2.) The design printed on the ferric salt may be developed by taking advantage of the reducing power of the exposed (ferrous) portions and the non-reducing power of the unexposed (ferric) portion. Thus with a solution of silver nitrate :—

$$2 Fe''_3 (C_6H_5O_7)_2 + 6 AgNO_3 = 4 Fe''' (C_6H_6O_7) + 2 Fe''' (NO_3)_3 + 3 Ag_2.$$
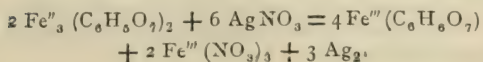
With a solution of auric chloride :—

$$2 Fe''_3 (C_6H_5O_7)_2 + 2 AuCl_3 = 2 Fe''' Cl_3 + 4 Fe''' (C_6H_5O_7) + Au_2.$$

Similarly with platinic chloride, chromates, mercury salts, and other reducible compounds.

(3.) Development can also be effected by utilising the oxidising property of the unexposed (ferric) portion, and the non-oxidising power of the reduced (ferrous) portion, such, *e.g.*, as by immersing in a solution of potassium iodide, mixed with starch paste.

Such demonstrations as these cannot fail to give a vivid idea of the effect of photochemical decomposition, and the striking results that can be obtained by the application of familiar reagents. It may be pointed out that the photochemical reduction of ferric salts, although practically useful for printing purposes, takes place too slowly to enable these compounds to be used at present for the production of camera pictures. But there is no reason why the rate of photochemical reduction—*i.e.* the sensitiveness of these compounds—should not be increased by admixture with some easily oxidisable substance and a sensitive film prepared by this means, which would cheapen photographic processes, by dispensing with the use of silver salts.

In the same way that the photo-chemistry of iron is studied, the other sensitive metallic compounds may be dealt with. The reduction of uranic salts, and the development of uranium prints by various reagents, will naturally be connected with the analogous ferric salts. The photochemical reduction of chromates in the presence of organic substances, such as gum, albumen, and gelatine, will lead to the numerous practical applications of chromated gelatine in the processes of etching, pigment printing, collotype, &c. In these processes practical instruction may be given at this stage as far as thought desirable. The salts of mercury and copper may also be studied with advantage, as illustrating the nature of photochemical decomposition. The well-known greenish mercurous iodide is easily prepared by decomposing freshly-precipitated and washed mercurous chloride with a solution of potassium iodide. Some of this salt, washed by decantation, and exposed under water to the action of strong light, rapidly darkens, owing to the liberation of metallic mercury. According to H. W. Vogel, the decomposition may be represented by the equation :—
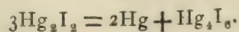
$$3Hg_2I_2 = 2Hg + Hg_4I_6.$$

The compound Hg_4I_6 is mercuroso-mercuric iodide, Hg_2I_2, $2 HgI_2$. The decomposition of mercuric chloride in the presence of ammonium oxalate is also an instructive illustration of photochemical decomposition, as it takes place with comparative rapidity, being the reaction made use of in Eder's chemical photometer :—

$$2 HgCl_2 + (NH_4)_2 C_2O_4 = Hg_2Cl_2 + 2 NH_4Cl + 2 CO_2.$$
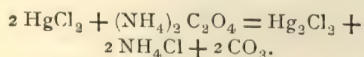
The action of light on the salts of copper forms a convenient introduction to the photochemistry of the silver salts. Thus cuprous chloride darkens, on exposure to light, with as great a rapidity as silver chloride. It may be pointed out that the nature of the decomposition in this case is not completely understood. Wöhler conjectured that the product might be an oxychloride, and this view receives support from the circumstance that cuprous chloride does not darken under hydrocarbon oils or other liquids which do not contain oxygen. A. Vogel assigns a formula $CuCl_2$, $3 CuO$, but the subject requires further investigation.*

A general discussion of the subject of photochemical decomposition, as illustrated by the foregoing and other examples, will enable the student of photographic chemistry to grasp the broad idea that modern photographic processes represent only the special applications of wider principles, and that photography with silver compounds may be but a passing phase in the history of the art. In the present state of knowledge, no rigorous classification of the cases of photochemical decomposition is possible, and it is only necessary to point out, and to illustrate by an appeal to some of the many known instances, how difficult it is to draw a hard and fast line between photochemical decomposition and photochemical combination, or between decomposition and dissociation under the influence of light. Many of the supposed cases of dissociation may be dependent on the presence of another substance capable of combining with one or the other of the liberated products, and thus playing the part of a sensitizer in relation to the present subject. From such considerations as these, it will follow that in all modern photographic processes we have to deal with a mixture of chemical compounds capable of passing into a more stable system under the influence of light as a source of external energy. If the

new products formed in this way are so acted upon by reagents subsequently applied that a visib'e and striking colour difference is produced, or if the new product differs in colour from the original substance or mixture of substances, we have all the essentials for a photographic method.

When discussing photochemical decomposition it should be pointed that indirect results are often obtained by using a mixture of substances of which one of the constituents is not directly affected by light, but is altered by contact with the product resulting from the photochemical decomposition of the other constituent of the mixture. For example, paper, coated with ferric chloride, and exposed to light, gives a surface of ferrous chloride by photochemical reduction, the size or cellulose of the paper acting as the sensitizer (chlorine absorbent). But if the surface is coated with a mixture of ferric chloride and cupric chloride, the ferrous chloride which is formed reduces the cupric salt with which it is in contact :—

$$2 FeCl_3 + 2 CuCl_2 = Cu_2Cl_2 + 2 FeCl_3.$$
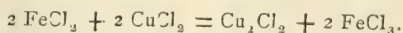
The picture is thus formed in cuprous chloride instead of in ferrous chloride, and, by treatment with potassium thiocyanate, cuprous thiocyanate is formed which, on subsequent treatment with potassium ferricyanide, leads to the development of a brown print. This method of utilising a mixture of ferric and cupric salts is the basis of Obernetter's process.

There can be no doubt that this principle of indirect decomposition is destined to play a very important part in the photography of the future. It has already come into prominence in the well-known platinotype process of Willis, in which a surface is coated with a mixture of ferric oxalate and potassium chloroplatinite. On exposure to light ferrous oxalate is formed, while the chloroplatinite is not directly reduced. On treatment with a hot solution of potassium oxalate the ferrous oxalate is dissolved out, and at the moment of solution reduces the chloroplatinite to finely-divided platinum *in situ*. In the direct printing platinotype process we have a surface of potassium chloroplatinite, sodium oxalate, and sodio-ferric oxalate. In this case the reduction of the ferric salt by light is accompanied by the indirect reduction of the chloroplatinite by means of the ferrous salt thus formed. In the cold platinotype of Willis the operations are separated, the ferric surface

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* See Dingler's " Poly. Journ.," vol. cxxxvi, p. 238 ; also Carlemann, in " Journ. für Prac. Chem.," vol. lxiii, p. 475.

being first exposed in the usual way, and then development being effected by immersion in a cold solution of potassium chloroplatinite containing potassium oxalate and phosphate.

The discussion and illustration of indirect methods of decomposition, as illustrated by the platinotype processes, may advantageously occupy the student's attention at this stage of his work. The chemistry is comparatively simple, and many experimental illustrations will obviously suggest themselves to the teacher.

LECTURE III.—DELIVERED MARCH 23, 1891.

The photochemical studies which have been dwelt upon in the last lecture lead up to the consideration of the silver compounds, which must of course receive special treatment on account of their present importance in photographic processes. The broad facts that silver nitrate darkens on exposure to light when in contact with organic matter, that the silver haloids become coloured when exposed under suitable conditions, and that other salts of silver, both inorganic and organic, also darken on exposure, will form the experimental basis from which the student may be led to the further consideration of the subject. At the outset of this work it is desirable to point out that our knowledge respecting the action of light on the silver compounds is in a different position to that concerning the simpler cases of photochemical decomposition which have hitherto been discussed. In the latter the chemical change is definite enough to be represented by ordinary equations, the composition of the final product being in most instances known. In the case of the silver salts we possess no such accurate knowledge, and the nature of the products is still surrounded by mystery.

When light falls on the silver haloids chemical decomposition takes place, accompanied by a change in colour. In order that this statement may be properly realised, let it be shown that there really is decomposition, and that the chloride and bromide under these circumstances give off a gas which blues starch and potassium iodide paper.[*] The iodide does not undergo decomposition on exposure except in the presence of an iodine absorbent, i.e., a sensitizer. From these facts a good lesson can be conveyed concerning the general nature of the action of sensitizers. Passing on to the action of light on films of the haloids, it is possible, by means of a few simple experiments, to demonstrate many important properties of these compounds with which the student should be familiar. For this purpose sheets of paper, well coated with the pure haloids free from excess of silver nitrate, and a few ordinary reagents, are the only requisites. By one operation it can be shown that with the same exposure the chloride becomes darker than the bromide and the latter darker than the iodide, and at the same time that reducing agents and halogen absorbents accelerate while oxidising agents retard the decomposition. Thus three strips coated respectively with the three haloids may be painted with stripes of solutions of (1) sodium nitrite, (2) sodium sulphite, (3) silver nitrate, (4) mercuric nitrate, (5) potassium dichromate. After exposing these strips simultaneously to the action of light, the stripes 1 and 2 will be darker than the ground-colour,

[*] " Chemistry of Photography," pp. 65–66.

showing the accelerating action of the reducing agents, 3 will also be darker than the ground-colour, showing that a halogen absorbent may also act as an accelerator without necessarily being a reducing agent, while 4 and 5 will retain the original colour of the haloid, showing the retarding action of oxidising agents. A comparison of the ground-colour in the three strips will also serve to show the different colours of the products of photochemical decomposition.

Such demonstrations as these cannot fail to impress the mind that the action of light on the silver haloids is a distinct case of photochemical decomposition, but it is necessary at this stage to issue a caution. The action is in these cases continued up to the point of visible darkening, whereas in the photographic film the exposure is so short that no directly visible effect is produced. It must be enforced therefore, that in associating the photographic image with these darkened products we are drawing largely upon arguments from analogy, and although I personally am inclined to the opinion that the products are the same in both cases, this view cannot be taught as a dogmatic truth in the present state of knowledge, for however probable it may appear from analogy it must not be forgotten that in the way of direct proof there is still a gap which must be bridged over before the identity of the products can be taught as an established fact. But the full consideration of this question is better deferred till the photographic film itself comes to be dealt with. The point that will now present itself is the actual composition of the darkened products, and here it may at once be pointed out to the student that our knowledge respecting these compounds is in precisely the same state as that concerning the coloured haloids dealt with in the last lecture. In the case of the darkened chloride, it has been proved that this product contains a little less chlorine than the normal chloride. In all three haloids, no matter how long the exposure may be, the final product always contains an enormous excess of unaltered haloid. It may safely be asserted that these products are not chemical compounds in the ordinary acceptation of the term, since they are not composed of the haloid combined with the coloured product of photochemical decomposition in definite molecular proportions.* Neither can the "photosalts" be classed

with the definite "molecular compounds" of modern chemistry, since the latter also consist of substances combined in definite molecular proportions, and can be more or less readily resolved into their constituent molecules by appropriate treatment. But the "photosalt" cannot be resolved by any such treatment, since all solvents which dissolve the normal haloid appear to decompose the darkened product, leaving only a trace of metallic silver. On the other hand, metallic silver cannot be extracted from the "photosalt" by any of the ordinary methods.

In answer to the question which the inquiring student would naturally put, what is the photosalt, it can only be said that these products must be regarded as indefinite molecular compounds of the silver haloids with coloured unstable products of photochemical decomposition, the composition of the latter being as yet unknown. That the coloured products are unstable appears from the fact that they cannot exist apart from an excess of the normal haloid. In the same way that a solvent will take up a solid till the point of saturation is reached, so the silver haloid, on exposure to light, becomes decomposed up to a certain point, $i.e.$, the point when the haloid is saturated with the coloured product of photo-decomposition.* Beyond this point the action of light produces no further effect unless a reducing agent is present capable of combining with the liberated halogen as fast as the latter is liberated. It is advisable to let the student observe for himself that silver iodide prepared with excess of potassium iodide undergoes no change of colour on exposure to light, but that in the presence of silver nitrate or reducing agents, darkening occurs. Let him observe also that the darkened chloride yields no appreciable quantity of silver to dilute nitric acid, but that in the presence of a strong reducing agent, even when the latter is gaseous, such as hydrogen, the reduction may proceed up to the complete liberation of the metallic silver. This last

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* It must be recognised that the definite character of molecular compounds passes into the indefinite when we have $\frac{1}{2} H_2O, \frac{1}{2} C_2H_4O_2, \frac{1}{2} CH_4O$, &c., in crystalline products.

* The analogy between a photosalt and a saturated solution was indicated in a lecture delivered last year at the Royal Institution ("Proc. Roy. Inst.," vol. xiii, p. 143). The idea of a "solid solution" may appear somewhat strained, and I am glad, therefore, of the present opportunity of calling attention to a similar idea which has occurred to others in connection with a totally different branch of chemistry, viz., the affinity of colouring matters for fabrics. This notion has been expressed by Dr. E. Knecht ("Journ. Soc. Dyers and Colourists," 1889, p. 77), and recently it has been extended with considerable force to the theory of dyeing by my friend Dr. Otto N. Witt ("Färber-Zeitung," 1890-91, Part I.).

point can be demonstrated very conveniently by placing some finely divided silver chloride (prepared by precipitation) into a glass tube through which a current of moist hydrogen is kept passing, the gas being made to bubble through a solution of silver nitrate containing free nitric acid. On exposing the contents of the tube for some time to strong light, silver chloride is precipitated from the solution of the nitrate, the chloride in the tube (which should be shaken from time to time in order to expose fresh portions) gradually becoming dark coloured. An equal quantity of the chloride may be exposed in air at the same time for comparison. The two lots of darkened chloride are then treated with equal quantities of dilute nitric acid, the clear solution filtered off, and the filtrates tested for silver. If the experiment has been properly conducted, the solution from the chloride darkened in hydrogen will be found to contain distinct traces, while that from the chloride darkened in air will be free from silver. It is hardly necessary to point out that the chloride used in this experiment should be free from excess of silver nitrate, i.e., prepared with an excess of a soluble chloride, or chlorhydric acid.*

Having arrived at the conclusion that the silver haloids, when exposed to light under suitable conditions, lose a small quantity of

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their halogen, and become converted into coloured compounds, the course of instruction will here naturally diverge along two lines :—

(1.) The nature of the coloured product combined with the excess of unaltered haloid ; and

(2.) The part played by the associated substance or sensitizer.

With regard to the first, it must be pointed out that, although we have no positive information of a conclusive character, many views have been advanced, which are more or less worthy of consideration ; and an excellent exercise in the use of scientific judgment might be given to the advanced student, by submitting the current notions respecting the composition of these products, and requesting him to prepare a critical essay embodying his own views. Although no definite conclusion might be arrived at, the exercise cannot fail to be of value as an educational test, not only by compelling the student to refer to original papers, but also as calculated to bring out any originality he may possess in the way of devising new crucial experiments—the highest criterion of competence as a technologist. Respecting the view that these compounds contain metallic silver, the fact that the chloride darkens under nitric acid may be taken as evidence to the contrary.* The discussion of the possibility that sub-haloids are present, will link this part of the subject on to the purely chemical considerations dealt with in the last lecture. The possibility of the coloured products containing oxygen, i.e., being of the nature of oxyhaloids, is also worthy of being entertained.† In favour of this view is the analogy of cuprous chloride, which darkens only in media which can supply oxygen, and which, under these circumstances, apparently forms an oxychloride. In the same sense may be interpreted the distinct sensitizing action of water already referred to. On the other hand, it may be pointed out, that the chloride darkens in a high vacuum (i.e., in the presence of mercury vapour), and under

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* The above experiment is a modification of one described by Robert Hunt (" Researches on Light," 2nd ed., p. 78). This method has recently been applied by R. Hitchcock (" Amer. Chem. Journ.," xi, p. 474), for determining quantitatively the loss of weight in films of silver chloride, exposed to light in an atmosphere of hydrogen. The author considers that his experiments prove that oxygen does not enter into the composition of the darkened product, i.e., that they disprove the oxychloride theory. But since water vapour was present, and was indeed found to be indispensable for the photo-decomposition, this inference cannot be allowed much weight. Moreover, since hydrogen is known to reduce the chloride to silver under the conditions of the experiment, the darkened product may have a different composition to that formed in air : it may consist of reduced silver, mixed with unaltered chloride. (See also C. H. Bothamley in " Brit. Journ. of Photog.," April 4th, 1890.) Hitchcock's films were prepared by allowing finely-divided silver chloride, obtained by precipitation, to subside on glass. (Herschel and Hunt's method). After being washed and dried under a dessicator, the films were but slightly darkened in dry air, even after an hour's exposure to bright sunlight. The introduction of water rapidly increased the rate of darkening, thus furnishing another illustration of the very familar fact that water acts as a sensitizer. This point was illustrated during the lecture by two experiments, conducted simultaneously. Strips of paper, coated with the chloride and bromide respectively, were partly screened by black paper, the exposed portions being partly wetted with distilled water. The chloride paper was allowed to remain exposed to the electric light till visibly coloured ; the bromide paper was withdrawn, after a few seconds and developed with weak ferrous oxalate developer. In both strips the portion wetted with water was distinctly darker than the exposed dry part of the coated paper.

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* Ostwald unhesitatingly affirms, both with respect to the wet collodion and gelatino-bromide emulsion processes, that traces of metallic silver are liberated by the action of light. (" Grundriss der allgemeinen Chemie," pp. 262-263.")

† According to a recent research by Dr. A. Richardson (" Journ. Chem. Soc.," vol. 59, p. 536), the chloride darkened under water does not contain oxygen. I learn, however, from Mr. H. B. Baker, of Dulwich College, that he has come to an opposite conclusion. His experiments are not yet completed, but he considers that the evidence in favour of the view that the darkened chloride contains oxygen is quite conclusive. He has measured the oxygen absorbed and the oxygen evolved by the action of chlorine on the darkened product.

liquids such as pure benzene, petroleum, and carbon tetrachloride, which contain no oxygen, and which have previously been dried by chemical methods. The question thus assumes the form, whether the nature of the coloured products may not vary in different media ; whether, in easily halogenised liquids, such as benzene, the reduction might not be analogous to that which occurs in hydrogen ; whether, in other cases, the unsaturated silver haloid residue may not form a coloured compound with the organic product ; and so forth. It may be pointed out that such questions as these open a wide and interesting field for experimental investigation.

With regard to the second point, the action of the substance associated with the silver haloid—it is legitimate to connect this action with the ordinary chemical processes with which the student has been familiarised. He has been taught that reduction and oxidation are concurrent in ordinary chemical reactions, such as when a silver salt is reduced by a ferrous salt. The principle can now be extended to photochemical reactions. With the exception of a few cases of pure dissociation (such as the resolution of gold oxide into metal and oxygen under the influence of light), which have no direct bearing on photographic processes, the photochemical changes with which the photographic chemist has to concern himself may all be considered from the same point of view as those which have been made use of by way of special illustrations. There is no fundamental difference in principle between the action of light on a mixture of ferric chloride and oxalic acid, or mercuric chloride and ammonium oxalate, and its action on a silver haloid mixed with water, silver nitrate, sodium sulphite, gelatine, or any other organic compound capable of being oxidised or halogenised. The only differences are in the relative velocities of chemical change, and in the circumstance that in the case of such metals as iron and mercury the products are definite and known, while in the case of silver the products are indefinite and unknown. The student will thus be led, without a break, from ordinary chemistry to photochemistry, and from the latter to the chemistry of photographic processes. He will now realise that the photographic film is to be looked upon as a system of chemical compounds capable of undergoing atomic rearrangement under the influence of the external energy of light. He will grasp the full meaning of the term "sensitizer," and he will see that the function of the latter is quite as important as that of the silver haloid itself.

From this point the practical study of photographic methods, the preparation of emulsions and films, the uses of collodion and gelatine as vehicles, the action of preservatives, and all the technical details of modern processes can be taken up or resumed. Then in natural sequence will follow the consideration of the nature of the photographic image and its connection with the coloured products resulting from the prolonged action of light on the silver haloids. At this stage, again, caution is necessary, and dogmatic statements must be avoided. The action of light on the sensitive films in use in photography, including all the films employed for producing pictures in the camera, from the iodised silver plate of Daguerre to the gelatino-bromide plate of modern times, gives rise to no visible product of photochemical decomposition. Is it therefore legitimate to conclude that the short exposure necessary to give a developable picture produces any photochemical decomposition at all ? It must be pointed out that there is here another gap in the way of direct proof, but that the indirect evidence is all in favour of there being such a chemical change. Of the nature of the material composing the invisible image we know no more than we do of the composition of the coloured products of photochemical decomposition, or of the photosalts. They may be identical or not ; but that the image is the result of a true chemical change can be made to appear highly probable to the student by a few well-chosen demonstrations. Let us consider the evidence as it stands.

The invisible image is either the product of chemical decomposition, or it is not. If it is not, then some other explanation must be invoked. The only other view is that the energy of light is not at first used up in doing chemical work, but that before true chemical decomposition occurs there is an intermediate stage, during which the energy is engaged in loosening the affinity between the atoms of the halogen and the silver. This would be analogous to Bunsen and Roscoe's "photochemical induction." According to this view we should have to regard the first action of light on the sensitive film as a purely physical action, resulting in the formation of an unstable modification of the silver haloid, more easily reducible than the ordinary modification. It might be thought that such a physical modification would be easily producible by the limited action of light on the pure silver haloid,

but as far as my own experiments have gone, this does not appear to be the case. By exposing pure, dry silver bromide films, obtained by the method already described, for sufficient time to produce a well-defined developable image on a photographic plate, no difference in the reducibility of the exposed and unexposed parts could be detected. In fact, the films of the pure haloid are so insensitive that an exposure to bright sunlight of sufficient duration to completely solarise the slowest of modern dry plates, showed no difference in reducibility by potassio-ferrous oxalate or alkaline-pyrogallol, between the exposed and unexposed portions of the surface. The conclusion to be drawn from these experiments is that in this form the silver haloid cannot be converted into a more easily reducible physical modification by any moderate exposure to light—certainly not by an exposure considerably greater than that necessary to impress an image on a gelatino-bromide plate.

At this point the question of molecular aggregation comes into consideration. Is it not possible that in the iodide film of the old collodion process, or in the gelatino-bromide emulsion, the silver haloid is in a different and more highly sensitive state of molecular aggregation? Is there, in fact, a more unstable condition of the haloid than that resulting from the action of the halogen on a silver mirror on glass? In considering this part of the subject attention may be called to the experiments which the student has already been recommended to make in connection with the modifications of the haloids. His experience in the preparation and ripening of emulsions will also render good service in enabling him to fairly consider the evidence. It is possible that some weight—how much it is not yet possible to decide—may have to be given to the state of aggregation as a factor in determining the extreme sensitiveness of the photographic film. At the same time it must be pointed out that no experimenter has ever yet succeeded in preparing a film of silver haloid in any state of aggregation free from every suspicion of a sensitizer, and capable of receiving an invisible and developable impression in the same time as an ordinary photographic plate.*

We are thus brought face to face with the remarkable fact that a film of pure dry haloid gives no product which is more easily reducible than the original haloid by any reasonable amount of exposure to light. Let the same haloid be diffused in fine particles throughout a sensitizing vehicle such as collodion (with the necessary preservative) or gelatine, and an exposure for a few seconds or a minute fraction of a second gives a product which is far more readily reducible than the unexposed haloid. It may be pointed out that it is extremely difficult to see where the necessity for invoking the physical theory of the photographic image comes in when these facts are fairly weighed.* The facts them-

very different from those which exist in a photographic film. It would be of interest and importance to reinvestigate this modification of AgBr from the photographic point of view. With reference to the production of an invisible image on a film of AgI on glass, opinions are divided (compare Abney, "Treatise on Photog.," 5th ed., p. 25, and Eder, "Handbuch," Part II., pp. 11 and 20). The authority for the statement that such an image can be produced is Carey Lea. In order to submit the question to the test of experiment I have made, with the co-operation of Mr. T. H. Norris, some further experiments with iodized silver mirrors on glass. The results with alkaline developers are the same as those with the brominated mirrors; there is no difference in reducibility between the exposed and the unexposed portions of the film. With an acid developer, however, a developable image is produced. A plate was half covered by a black screen and the uncovered portion exposed for five minutes to the light of the electric arc. The developer was the ordinary pyrogallol solution with acetic acid as a restrainer and a few drops of $AgNO_3$ solution. The silver deposit formed on the exposed portion long before the unexposed half was attacked. This confirms Carey Lea's results, and at the same time opens up a very wide question, viz., whether photochemical decomposition is necessary for development by accretion as distinguished from development by reduction. It may be that photophysical change is competent to give an image capable of accretional development. It is known that the silver haloid when crystalline is susceptible of photophysical change (Schultz-Sellack, Pogg. Ann., vol. 143, p. 439).

* In his inaugural address to the Photographic Section of the Liverpool Physical Society (Jan. 19th, 1891, "Photography;" Feb. 19th and 29th, 1891), Dr. F. Hurter states that it has always appeared impossible to him "to reconcile the short exposures necessary for the production of photographic images with any theory which demanded the absolute separation of the halogen, or part of it, from the silver." He bases his objections to this (chemical) theory on quantitative experiments, which go to prove that the energy supplied by the initial source of light is totally inadequate to account for the decomposition of the haloid, or the quantity of silver produced on the film by subsequent development. It does not appear to me, however, that these experiments or calculations in any way affect the chemical theory of the photographic image. The actual amount of photochemical decomposition, as measured by the quantity of silver produced on reduction may be, as the author states, connected with the initial source of energy by a logarithmic law. But this does not prove that no separation of halogen takes place; the energy is not to be regarded as acting upon AgBr alone, but upon a most intimate mixture or possibly even upon a compound of AgBr and gelatine. The latter substance is well known to combine with bromine to a very con-

* According to Stas the third (granular) modification of AgBr (both the white and yellow forms) are extremely sensitive to light. He states that on boiling (with water?) in a glass flask they become darkened in two or three seconds by the blue flame of a Bunsen burner. It is not clear from the description whether he attributes the darkening to the light of the burner alone, but the conditions are obviously

selves can be easily demonstrated without any appeal to a photographic plate. It is only necessary to take one of the brominated silver mirrors and streak it with a dilute solution of gelatine, allowing the solution to remain for 10 or 15 minutes in contact with the film. The gelatine stripes can, if necessary, be kept moist by adding water from time to time. The plate is then exposed to strong light for a few seconds, washed with warm water to remove the excess of gelatine, and then developed with a weak ferrous oxalate solution containing plenty of potassium bromide. If the experiment has been properly made the stripe under the gelatine develops before the remainder of the film is attacked.

From this and many analogous experiments which might be made or quoted,* it will be made clear to the student that the function of the sensitizing vehicle is of a very high order of importance. It will be seen also that the particular vehicle now in vogue, gelatine, is a particularly good sensitizer, and it is legitimate to connect its sensitizing action with its well-known power of taking up bromine. It may be asked whether it is more probable that mere contact with a solution of gelatine should so alter the physical condition of the haloid (as in the last experiment) as to convert it from a comparatively insensitive to a highly sensitive physical modification, or whether it is more probable that the gelatine should act in the same way as the reducing agents used as sensitizers in the former experiment with the coated papers. It may, I think, be fairly taught that the balance of probability is in favour of the purely chemical action of the gelatine. In accordance with this view is the fact that no collodion emulsion, however the haloid may be modified in physical condition by "ripening," can be made as rapid as a modern dry plate. On the other hand, in favour of the view that some weight must be given to the state of aggregation, it may be pointed out that the silver bromide on glass, although considerably increased in sensitiveness by contact with a gelatine solution, is still much less sensitive than the emulsion.

If, therefore, it is regarded as improbable

that mere contact with a gelatine solution can alter the physical condition of the haloid, it may be asked what happens during the ripening of an emulsion. The student will have learnt that when silver bromide is first precipitated in gelatine, the emulsion is comparatively insensitive. It is only by long contact with the gelatine solution at the ordinary temperature, or by the action of heat for a shorter period, that the emulsion acquires its maximum sensitiveness. It is believed by the majority of photographic chemists that the change which occurs during this process is a purely physical one—that there is a growth in size of the particles accompanied by corresponding changes in optical properties.* As already stated, it is possible that some such physical change of condition may occur, and that the increase of sensitiveness may be partly attributable thereto. The condition of the bromide particles in an emulsion is, from the beginning, very different from the condition of the bromide on a film prepared by brominating a silver mirror on glass. Nevertheless, I do not believe that we are at present justified in teaching dogmatically that the whole increase in sensitiveness is due to physical modification only. I must confess that, from experiments which I have been making, and which I hope at some future time to continue, that I am gradually coming round to the view that more and more weight must be given to the probability of combination between the silver haloid and the gelatine, and less weight to the state of molecular aggregation than has hitherto been conceded. If analogy is wanted in support of this view, it is only necessary to remind you of the existence of the " gelatino nitrate " of silver prepared in a former experiment. If gelatine can combine with silver nitrate to form a compound capable of photochemical decomposition, it is not unreasonable to suppose that a similar kind of compound might be formed from a silver haloid and gelatine, or some constituent of the gelatine, under the conditions essential for ripening an emulsion. It is desirable that the photographic chemist should be prepared for the proof, which may be at any time forthcoming, that the marvellous sensitiveness of the modern dry plate is not altogether due to the particular state of aggregation of the silver haloid, but that the substance which is so sensitive to light is an organic silver haloid compound belonging to that indefinite " molecular "

siderable extent (20·5—22·9 p.c.; see Weyl in Chem. Centralbl. 1878, p. 198, and Knop, *ibid*, 1879. The action of light on the photographic film is rather comparable with the action of heat on an explosive mixture or compound ; the total energy evolved on the explosion of gunpowder is not dependent on the amount of energy supplied by the spark which determines the explosion.

* See Sect. III. of chap. x. of Eder's " Ausführl. Handb.," Part III.

* For further particulars, see " Chemistry of Photography," pp. 120 132.

group so frequently met with in this branch of chemistry.

From this stage onward, the practical study of photographic processes may be carried on hand in hand with the demonstration of the chemical principles concerned. The photographic image will be regarded as being most probably composed of a product of true photochemical decomposition. This product may, or may not, be identical with the " photosalts," but it is not improbable that its composition may vary according to the nature of the vehicle with which the silver haloid is associated. The sensitive film which is now in general use will be regarded as a " gelatinobromide," in the same sense that the term " gelatino-nitrate " has been employed. The photographic image will be looked upon as a design on the surface of the gelatinobromide, composed of a chemical product more easily reducible than the gelatinobromide, and invisible simply because of the extreme tenuity of the deposit. When a reducing agent is applied, the material composing the invisible image is alone reduced to metallic silver,* and the picture is said to be "developed." The subject of development may now be dealt with, and the chemical principles of the process demonstrated. It is necessary to commence by pointing out that a photographic developer may act in two distinct ways. In development by vapour, as in the Daguerreotype, and in the so-called acid developers, there is an accumulation of finely-divided metal (resulting from condensation in the case of mercury vapour, and from chemical reduction in the case of acid developers) on the material of the invisible image only. If, for example, silver nitrate is reduced by ferrous sulphate or pyrogallol, the pulverulent deposit of metal accumulates by preference on the product of photochemical action, and continues to be deposited thereon as long as there is silver being deposited from the developing solution. Where the silver deposit has once formed, there it continues to grow by accretion, and the developed picture is built up of metallic silver. The action is, doubtless, of an electrolytic character, the material of the invisible image, and the unaltered haloid forming the two elements of a galvanic couple, and the developing solution playing the part of the electrolyte. To illustrate the mode of action of developers of this class, it is only necessary to use one of the silver on paper designs produced as in the first lecture. An extremely faint design in reduced silver, on being immersed in a solution depositing the metal by reduction, becomes darker and darker by the process of accretion. In order to broaden the student's notions, it must be pointed out, and illustrated experimentally, that this process is not peculiar to silver. A design in any freely-divided metal, such as mercury, gold, or platinum, produced by reduction (chemical or photochemical) on a paper surface can be "developed" in the same metal, by immersing it in the solution from which the metal is being deposited by chemical reduction.

The other kind of development effected by such reagents as ferrous oxalate, alkaline pyrogallol, eikonogen, and hydroquinone, must be regarded as also due to reduction: but, in these cases, it is the material composing the invisible image which is directly reduced. This constitutes the so-called alkaline development. It must be taught, in connection with this subject, that the silver deposit which results from the reduction of the invisible image is not the exact equivalent of the quantity of material composing that image, but that the reduction commenced on the portions exposed to light extends downwards through the film as long as the developer is acting. In fact, it must be made clear that the silver deposit *grows* by continued reduction, the action in this case also being most probably electrolytic, the elements being the first film of reduced silver, the unchanged haloid with which it is in contact, and the developing solution as the conducting medium.

The final result of both kinds of development is the production of a silver picture, composed of far more silver than can be accounted for by the actual quantity of the material composing the invisible image. The two kinds of development may be classified as "accretional" and "reductional" (chemical and physical, according to the Continental photographers). The broad principles of the process having

* It is well known that a reducing agent of sufficient strength to reduce silver bromide directly, such as the ordinary ferrous oxalate developer, may be applied with a gelatino-bromide dry plate. It is generally taught that the haloid is protected in such an emulsion by virtue of the particles being imbedded in the gelatine. I am disposed to believe, however, that the protection is not merely physical, but that the weak chemical combination between the haloid and the gelatine (or one of its constituents) results in the formation of a compound less reducible than the haloid itself. I may point out, incidentally, that the change in size of the particles, and the modification in optical properties undergone by the emulsion during the process of ripening, as well as the increase in sensitiveness, are all in accordance with the chemical theory of the gelatino-bromide film.

been elucidated, the student may proceed to the study of the individual developers, their mode of preparation, and the probable chemical changes which they undergo when acting upon an exposed plate. In dealing with the latter point, it is not essential that the actual composition of the material composing the invisible image should be known; it is only necessary to regard the action as occurring between free halogen and the reducing agent in the presence of water. In the case of such a developer as ferrous oxalate the chemical change is sufficiently obvious, but the action of halogens and water upon organic reducers is far less definite, and it will be safer to abandon all attempts to represent the changes by equations in the present state of knowledge. It may be less satisfactory, but it is a more truly scientific attitude to confess imperfect knowledge than to invent nicely balanced equations which may be quite remote from the truth.

Having mastered the principles of development, it is important that the student should have his attention directed to certain phenomena which connect this subject with the initial action of light on the photographic film. He will have learnt from the previous demonstrations that the photographic image with which he is practically familiar is most probably a product of photochemical decomposition. He will thus be prepared for the proof that chemical reducing agents may act in the same way as light; that is to say, that by employing a very slow reducer and allowing it to act on the silver bromide for a short time, the reduction is carried to the same stage as that which results from the initial action of light. The process of reduction can be arrested at the invisible stage—at a stage intermediate between the haloid and the free metal. The product thus formed, whatever its composition may be, is more easily reducible than the original haloid, and can therefore be "developed" by ferrous oxalate, &c., in just the same way as the invisible image. The simplest way of showing this is to stripe a sheet of paper coated with the haloid with an alkaline solution of glucose, allow the latter to act for a few minutes, wash thoroughly, and then develop with weak ferrous oxalate containing plenty of soluble bromide. It may be pointed out that such a result as this, for the experimental demonstration of which we are indebted to Carey Lea, is opposed to the physical theory of the photographic image, since it is difficult to see how the mere contact

of a silver haloid with a feeble reducing agent can modify the physical stability of the haloid so as to transform it into a chemically unstable modification.

Another fact bearing on the present subject which must not be overlooked, is that mechanical force of the nature of a shearing stress also produces a developable impression on a silver haloid film. So far as my experiments have gone, this result cannot be produced except in the presence of a sensitizer; any of the ordinary photographic films will show it, but I have thus far been unsuccessful with the halogenised mirrors on glass. Although negative evidence does not count for much, it appears thus far that the effect is only producible under the same conditions that an invisible image is produced by light. If this be so, then we have an additional argument in favour of the chemical theory of the photographic image, for the researches of Prof. Spring of Liege have shown that a mixture of compounds can be made to undergo chemical interaction by mechanical pressure alone. The silver haloid and its associated or combined sensitizer provides such a mixture or compound.

In connection with the necessarily related subjects of exposure and development, the phenomenon of reversal must be dealt with. I regret exceedingly that time is pressing me towards a conclusion, and that I can do no more than hint at the mode of treatment of this important subject. I have already expressed the view* that this phenomenon is best regarded as reversed chemical action between the halogenised sensitizer and the material of the invisible image. Since that view was put forward three years ago, no new facts have been adduced which are in opposition to it, and I am therefore bold enough to think that it is at any rate worthy of being taken into consideration by the teacher of photographic chemistry. In the broadest possible terms all that we have to consider is that the "photosalt" in contact with a sensitizer containing more than a certain quantity of halogenising or oxidising material has the tables turned upon it, to speak metaphorically, and then acts as a sensitizer towards the film which at first acted as a sensitizer towards it. The principle can be demonstrated by utilising a very old experiment. It is known that potassium iodide is capable of undergoing photochemical oxidation in the presence of moisture and air; iodine and potassium hydroxide are

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* "Chemistry of Photography," pp. 209-230.

formed, and of course interact in the absence of some other iodine absorbent. A photosalt is an iodine absorbent, and therefore if a sheet of paper be coated with a silver haloid, and then exposed to light till it darkens, we have a surface capable of sensitising a solution of potassium iodide, so that the latter undergoes photochemical oxidation with extreme rapidity, the liberated iodine being absorbed by the photosalt which thereby becomes bleached, *i.e.*, converted into the ordinary haloid.

Having brought the student up to this stage of knowledge, we must leave him in possession of a silver picture produced by development, and the chemistry of the subsequent operations of fixing, clearing, intensifying or reducing, printing, toning, and so forth, will be comparatively simple, after the course through which he is supposed to have been conducted. With regard to these subsequent operations, all that has to be borne in mind is that, after fixing and washing, the image is composed of a graduated deposit of metallic silver, and that all the changes that are wrought upon it by intensifiers or reducers are simply the result of ordinary chemical transformations. Thus the principle of intensification may be demonstrated in the usual way, viz., by producing a design in silver on paper, as in the first lecture, then bleaching it by immersion in a solution of mercuric chloride, and,

after washing, converting the mercurous chloride formed into the dark dimercurous ammonium chloride. The final result is a more opaque image—the latter has become intensified.

I have, perforce, been obliged to keep rigidly to my programme in this course of lectures ; there has been no time for straying into bye-paths, and I have confined myself strictly to the chemical aspect of the subject. I said, at starting, that it has also its physical side and the special action of the spectrum colours on the different photo-sensitive compounds, the electrical phenomena accompanying development, the action of special sensitizers in connection with orthochromatic photography, the subject of heliochromy, &c., must be included in every complete course of instruction in photographic technology. It has been my object to indicate the general lines on which this branch of technical training should be conducted ; the teacher will no doubt discount the personal element from these lectures as far as he may think desirable, and after he has done this, if he will conduct the student along the broad track, towards which I have acted the part of a finger-post, we may call into existence a race of technologists who will raise the subject of photography to that high position as a science which it has already taken as an art.